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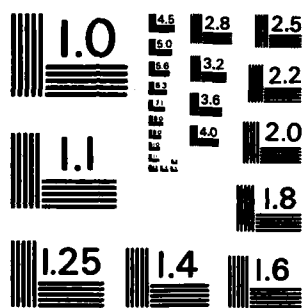
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**Tricresyl Phosphate Retention by
Bearing Retainer and Reservoir Materials**

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16 July 1984

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


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Project Officer


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Tricresyl phosphate (TCP) is an important extreme-pressure additive in lubricating oils. Its depletion from reservoir oil could constitute a failure mechanism for bearing systems. The interaction of TCP with bearing retainer and reservoir materials was investigated using an apparatus that mimicked centrifugal oil feed. TCP was not selectively absorbed by cotton-phenolic retainer or wool felt reservoir materials, but was absorbed by nitrile-acrylic and sintered nylon reservoir materials, which exhibited		

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significant TCP retention. The results are discussed in terms of the degree of bulk oil absorption, the availability of polar sites on the sorbents, and the interaction between such sites and the TCP molecules.

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PREFACE

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I. INTRODUCTION

Lubricant reservoirs and some bearing retainers are constructed of polymeric materials. In their intended applications, such devices must, over extended periods and many times under centrifugal force, deliver lubricant to the bearings. It is important that the interaction of the lubricant with these polymeric materials does not result in the alteration of the lubricant through physical and chemical processes. Of particular concern is that the extreme-pressure (EP) additive, tricresyl phosphate (TCP), might be selectively retained from a mineral oil lubricant by various bearing reservoir and retainer materials. Since the long-term effectiveness of TCP depends on the lubricant's replenishment of any material that is worn away, depletion of TCP from the reservoir oil could constitute a potential failure mechanism for the bearing system.

The results of a study by Gardos et al. indicated that TCP was preferentially retained on phenolic and polyimide retainer materials.¹ That study employed a chromatographic method in which the additive-containing oil was eluted through a packed column using n-hexane solvent. The column packing consisted of pulverized retainer materials.

Our application focuses on a centrifugal feed mechanism that would not be mimicked by the chromatographic elution approach. As a result, four retainer/reservoir materials were investigated: wool felt, cotton-phenolic, nitrile-acrylic polymer, and a sintered nylon polyamide. In the investigation, the retention of TCP was measured for the four materials, and studies of gas permeability and oil absorption were performed on the phenolic to determine the role of bulk absorption in oil additive retention phenomena for that material.

II. EXPERIMENTAL

A. SAMPLE PREPARATION

The cotton-phenolic and wool felt used for the TCP retention measurements were space-qualified and were not further treated. The cotton-phenolic used for the helium permeability and oil impregnation studies was not space-qualified and was tested both as received and after Soxhlet extraction. The nylon was Soxhlet-extracted with methanol. The nitrile-acrylic was washed twice in hot water to remove the salts that were present during processing. The wool felt was cut into $4 \times 2 \times 1$ -mm pieces. The cotton-phenolic, nylon, and nitrile-acrylic materials were pulverized by drilling and filing. Most materials were used directly, except for the phenolic, which was passed through a 60-mesh sieve before use. The oil, containing approximately 1 weight percent TCP, is a commercially available, highly refined mineral oil. The TCP is just one component in the additive package. For each experiment, 0.3 to 0.4 g of sorbent and 0.4 to 0.5 g of oil were used.

B. TCP-SORBENT INTERACTION

The centrifugal feed mechanism was simulated with special centrifuge glassware and a centrifuge. The glassware consisted of two glass containers separated by a glass frit (Fig. 1). The oil was distributed onto the retainer/reservoir sample in the upper container. After allowing several days for the TCP to partition between the oil and sorbent and to reach equilibrium, the apparatus was centrifuged, forcing the liquid from the upper container into the collection vial.

C. TCP ANALYSIS PROCEDURE

Samples were prepared for analysis by extracting the centrifuge eluants with ethanol (>97 percent TCP extraction from the oil), then the ethanol solutions for all samples were analyzed by colorimetric procedures. The phenolic and blank-sample ethanol solutions were also analyzed using high-performance liquid chromatography (HPLC).

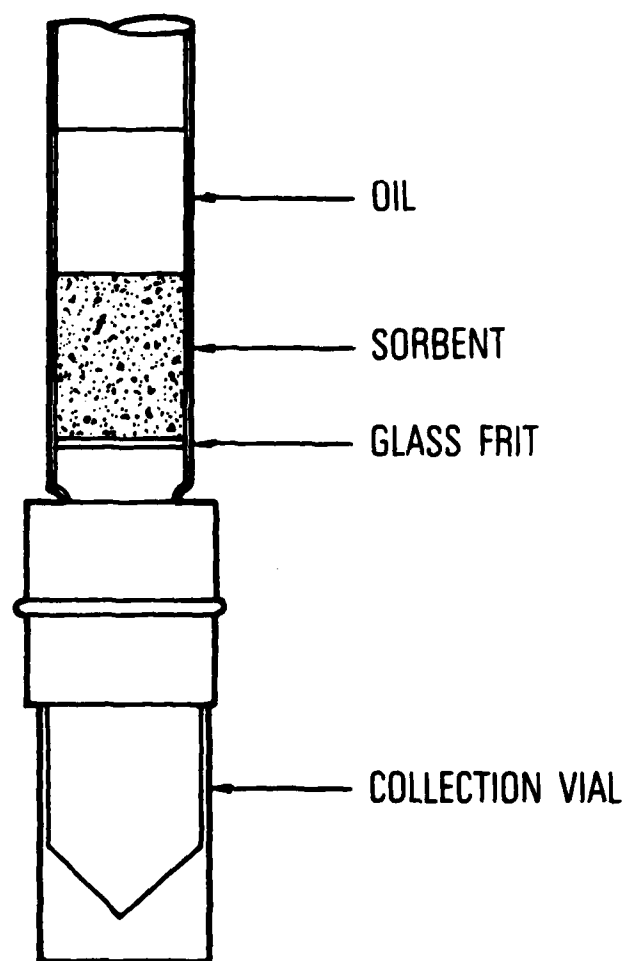


Fig. 1. Special centrifuge glassware and sorption test configuration (not to scale).

1. COLORIMETRIC ANALYSIS

The ethanol was evaporated from the samples, after which the residue was digested by a nitric acid-sulfuric acid mixture to convert the TCP to phosphate ion. The phosphate ion concentration was determined using a commercially available phosphate detection reagent. In the presence of phosphate ion, a blue color develops. The absorbance of the solution at 750 nm, which is proportional to the phosphate ion concentration, was measured spectrophotometrically. Calibration of the reagents resulted in a calculated sensitivity of 0.001 volume percent of TCP in the oil.

2. HPLC ANALYSIS

The HPLC was operated in the gel permeation chromatography mode. The separation is achieved by size exclusion, in which the sample's components are separated as a function of molecular size, which is approximately proportional to molecular weight. The following instrumental conditions were used:

Columns:	Two 100-Å styrene/divinylbenzene copolymer solid phase
Solvent:	Ethanol
Flow Rate:	0.5 ml/min
Sample Size:	20-μL fixed loop injection of ~ 1 weight percent TCP in ethanol
Detector:	Refractive index (RI)

The samples were prepared by volumetric dilution with ethanol. The RI detector response was calibrated against known solutions of TCP in ethanol. The detection limit for this procedure was determined to be 0.2 percent TCP in mineral oil.

D. HELIUM PERMEABILITY

A piece of cotton-reinforced phenolic material was cut into a tube-shaped piece that was 51.7 mm thick, with an inner diameter of 41.3 mm and an outer diameter of 50.8 mm. Stainless steel end plates were machined to fit the ends of the tube, and one end piece was fitted so that it could be connected to a portable leak detector that was tuned and calibrated for helium with a standard leak of $2 \times 10^{-8} \text{ cm}^3 \cdot \text{atm} \cdot \text{sec}^{-1}$. A high-vacuum silicone sealant

ensured a tight seal in the end pieces. (The test setup is shown in Fig. 2.) Leakage measurements were taken while the entire assembly was being sprayed with helium, and the assembly was bagged and pressurized to 110.32 kPa (16 psi) with helium. No leakage was detected. The phenolic tube was extracted with solvent and retested. Material was machined off the inside, outside, and ends, and the piece was retested. No leakage was detected under any of the conditions. The lower detection limit was $5 \times 10^{-9} \text{ cm}^3 \cdot \text{atm} \cdot \text{sec}^{-1}$.

E. VACUUM OIL IMPREGNATION

Pieces of phenolic were suspended above the oil in a bell jar at a pressure of 10^{-4} Pa. After sufficient time was allowed for trapped air to escape from the phenolic and for the oil to degas, the phenolic piece was dropped into the oil, where it remained for up to 100 h under vacuum. (The oil temperature was maintained at about 60°C during the impregnation.) The phenolic piece was removed from the oil, the excess oil was removed by centrifuging the phenolic, and the piece was weighed. The weight percent oil was the difference in weight of the phenolic before and after oil impregnation.

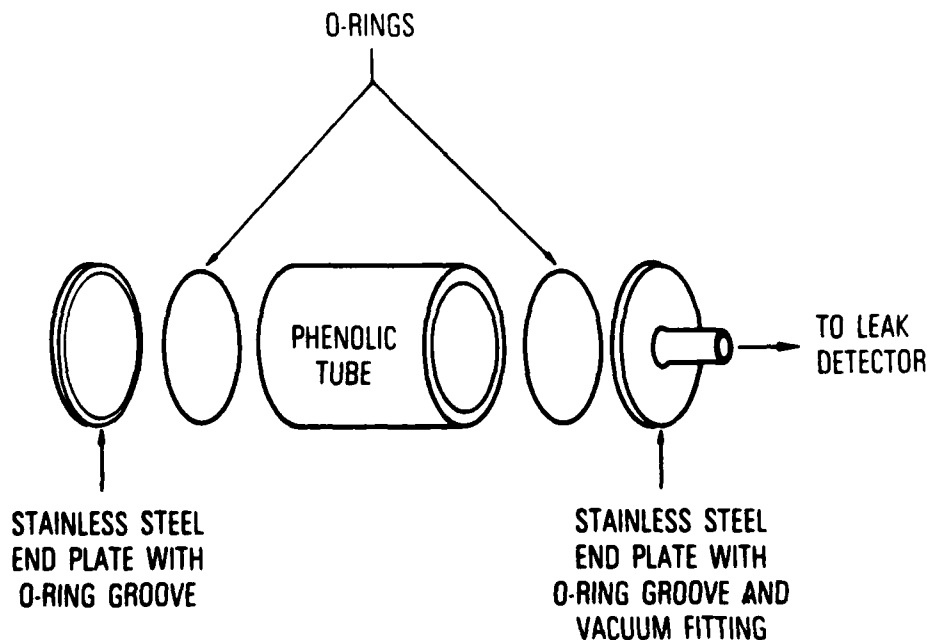


Fig. 2. Phenolic helium permeability test setup, exploded view (not actual size).

III. RESULTS AND DISCUSSION

The sorption experiment results are presented in Table 1. The cotton-phenolic and wool felt exhibited no TCP retention, whereas the nitrile-acrylic and sintered nylon exhibited significant TCP retention. The cotton-phenolic results will be discussed first, followed by a discussion pertaining to the other materials.

TABLE 1. TCP ANALYSIS RESULTS

Substrate	Number of Determinations	TCP, weight percent	
		Colorimetric	HPLC
Wool felt	4	1.06 \pm 0.16	
Cotton-phenolic	5	1.16 \pm 0.16	1.16 \pm 0.11
Nitrile-acrylic	4	0.24 \pm 0.07	
Sintered nylon polyamide	4	0.35 \pm 0.14	
Blank oil	5	1.10 \pm 0.14	1.18 \pm 0.03

A. COTTON-PHENOLIC

Within the analysis uncertainty of this study, no sorption of TCP by phenolic occurred. However, an understanding of the degree of adsorption on the external surfaces and absorption into the bulk and our ability to detect either is required to interpret the results. The particles used were 60 mesh ($\sim 250 \mu\text{m}$ in diameter), which would give a total surface area of about 100 cm^2 (the surface areas of actual retainers are much smaller) for 0.4 g of phenolic material, assuming a phenolic density of 1.0. Estimating one monolayer coverage of TCP molecules to be $2 \times 10^{14} \text{ molecules} \cdot \text{cm}^{-2}$, the total adsorbed TCP would be about 0.2 percent of the TCP in 0.5 ml of the 1 percent solution.

Thus, even if monolayer surface coverage by TCP had occurred, detection would have been impossible, because our standard deviations were much larger than the maximum quantity of TCP that could be adsorbed.

In the previous work, 50 times more sorbent of the same approximate particle size was employed.¹ With 0.5 ml of the 1 percent TCP solution used, a maximum of approximately 10 percent of the TCP could be involved in surface adsorption. Under such conditions, adsorption of TCP would be detectable and may have been responsible for their observations. Because only small amounts of TCP could be retained through surface adsorption in normal retainer geometries, this mechanism of TCP sorption is not of concern.

The possibility of bulk TCP absorption was investigated by permeation techniques. Helium permeability was measured for three phenolic samples--as received, after Soxhlet extraction, and after machining down the ends that were previously exposed--but none was detected. The minimum detection limit in our experiment was $5 \times 10^{-9} \text{ cm}^3 \cdot \text{atm} \cdot \text{sec}^{-1}$. Using this value as an upper limit, and using the substrate geometry and helium pressure, the maximum calculated helium permeability is $2.4 \times 10^{-13} \text{ cm}^3 \cdot \text{atm} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{cm(Hg)} \cdot \text{sec}^{-1}$, a value four to five orders of magnitude smaller than the helium permeabilities of common elastomers and polymers.² In addition, oil permeabilities are smaller than helium permeabilities.^{2,3} Thus, there would be no significant bulk absorption of TCP by the phenolic material.

Sorption of oil by cotton-reinforced phenolic material must occur by the capillary action of the cotton fibers whose cross sections are exposed by machining. Vacuum impregnation techniques were used to determine whether sorption of oil by that mechanism could cause anomalous retention of TCP. (During the pulverizing, the phenolic and cotton would be separated and the cotton removed by sieving. Thus, the participation of the cotton in the absorption phenomenon would not be tested using pulverized sorbent.) Following vacuum impregnation, the maximum quantity of oil retained by the phenolic material was about 2 weight percent relative to the weight of the phenolic sample. The postimpregnation samples were cut and examined by fluorescence for oil penetration. (Some oil additives and impurities

fluoresce in the visible wavelength region when excited with ultraviolet radiation of the appropriate wavelength.) The oil did not penetrate significantly into the bulk of the phenolic material. Thus, retention of TCP by phenolic retainers through bulk absorption can be concluded not to be a serious concern.

B. WOOL FELT, NITRILE-ACRYLIC, AND SINTERED NYLON

The remaining TCP analysis values in Table 1 are for the reservoir materials: wool felt, sintered nylon, and nitrile-acrylic. The wool felt did not retain the TCP, whereas the sintered nylon and nitrile-acrylic exhibited significant TCP retention. Gardos et al. argued that retention of TCP was due to interactions between the polar TCP molecules and polar sites on the sorbents, either hydrogen bonding or dipole-dipole interactions acting to bind the TCP molecules.¹ Wheeler and Faut have proposed that dipole-induced dipole interactions may be responsible for the adsorption of TCP on gold.⁴ Such interactions may account for our results.

The sintered nylon and nitrile-acrylic materials are synthetic, and the polymer chains interact with each other by forming hydrogen bonds or dipole-dipole attractions.⁵ On the surface, the outer chains may contain exposed polar groups that can interact with TCP. Wool, on the other hand, is a naturally occurring α -keratin material that forms α helices with intramolecular hydrogen bonding holding the helical conformation^{5,6}--leaving no exposed sites for interaction with TCP. Although water can penetrate and uncoil the α helix,⁵ the TCP molecule is too large to penetrate the α helix and interact at the sterically hindered reaction sites. We have no other hypotheses to account for our experimental observations.

IV. CONCLUSIONS

The following conclusions can be drawn from the experimental results:

1. TCP sorption by cotton-reinforced phenolic retainer material is not significant.
2. Wool felt reservoir material does not retain TCP, whereas nitrile-acrylic and sintered nylon exhibit significant TCP retention.

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